

Solubility, speciation and solid phase formation of Pu(VI) in alkaline CaCl₂ and NaCl solutions

A. Kuzenkova¹, D. Fellhauer², D. Schild², X. Gaona², J. Rothe², A. Romanchuk¹, S. Kalmykov¹, M. Altmaier²

¹ Lomonosov Moscow State University, Moscow, Russia

² Karlsruhe Institute of Technology-Institute for Nuclear Waste Disposal (INE), Karlsruhe, Germany

INTRODUCTION

Within the An(VI) series, the hydrolysis behavior of Pu(VI) in aqueous solution shows some unique features that are clearly different from that of U(VI) and Np(VI). While U(VI) and Np(VI) readily form sparingly soluble An(VI)-(hydr)oxide solid phases in neutral to alkaline solutions, e.g. AnO₂(OH)₂·xH₂O(cr), Na₂An₂O₇·xH₂O(cr) with An = U [1] and Np [2], and CaU₂O₇·3H₂O(cr) [3, 4], the hydrolytic behavior of Pu(VI) is dominated by the formation of dissolved polymeric hydrolysis products (PuO₂)_y(OH)_{x2y-x}(aq). The latter are metastable, even at relatively high [Pu(VI)]_{tot} [5], which becomes evident in the sluggish formation of Pu(VI)-(hydr)oxides. This challenge can explain why little is reported about the solubility behavior of Pu(VI)-(hydr)oxides. In this contribution we report on the successful preparation, characterization and solubility analysis of some Pu(VI)-(hydr)oxide solid phases in alkaline NaCl and CaCl₂ solutions.

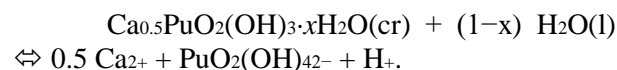
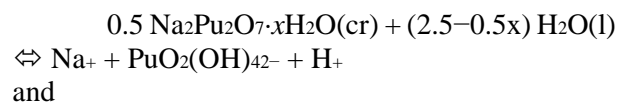
DESCRIPTION OF THE WORK

All experiments were performed at room temperature under inert Ar atmosphere with ²⁴²Pu. A freshly electrolyzed oxidation state pure ²⁴²PuO₂₂₊ stock solution was alkalized with NaOH and with aqueous Ca(OH)₂ suspension, respectively. Mild tempering for several weeks resulted in the formation of blackish (Na) and yellow-brownish (Ca) crystalline precipitates. The latter were investigated by powder XRD, SEM-EDX, chemical analysis by combined LSC+OES, Raman, thermogravimetric analysis, and XAFS at the *Karlsruhe Research Accelerator* (KARA). The solubility behavior were studied in 0.5-5.0 M NaCl solutions with pH_m = 9-14 (blackish solid) and 0.25-2.0 M CaCl₂ solutions with pH_m = 9-12 (yellow-brownish solid phase) from undersaturation using hypochlorite as oxidizing agent. Several samplings of pH_m = -log [H⁺]_m (glass combination electrode), [Pu]_{tot} (LSC) and [Pu(VI)] (liquid extraction) were performed as a function of time. Additional spectroscopic

(Vis/NIR, EXAFS) investigations of the aqueous Pu(VI) speciation were performed.

RESULTS AND DISCUSSION

The results of the solid phase characterization shows that the blackish material precipitated in NaOH solution is a plutonate(VI) compound and consists of hexagonal platelets (SEM). Chemical analysis by EDX and by LSC+OES revealed an equimolar content of Na and Pu in the solid (Na : Pu ≈ 1:1). The compound is isostructural to Na₂An₂O₇·xH₂O(cr) with An = U [1] and Np [2] as confirmed by powder XRD. The blackish solid phase can therefore be identified as Na₂Pu₂O₇·xH₂O(cr). The yellow-brownish Pu(VI) solid phase precipitated in Ca(OH)₂ solution consists of small rods (SEM) with a Ca : Pu ratio of 0.5 : 1 (EDX). Based on the XRD pattern, the solid phase is not isostructural with the uranate(VI)-like CaU₂O₇·3H₂O(cr) (hexagonal platelets) reported in [3]. The results are in agreement with an empirical formula Ca_{0.5}PuO₂(OH)₃·xH₂O(cr) (plutonyl(VI)-like structure). Thermogravimetric analysis of both solid phases to determine the content of crystal water will be performed at the end of the solubility study. Based on the initial data, both solid phases show a systematic increase of the Pu(VI) solubility with slope ≈ +1 for pH_m ≥ 11.5 which can be explained by PuO₂(OH)₄₂₋ as predominant Pu(VI) aqueous species under these conditions:



For U(VI) (and Np(VI) in NaCl solutions), an analogous behaviour was observed [1, 2]. Details of the solubility behaviour, especially the data obtained for the less alkaline region, and from the results of additional solution Vis/NIR investigations will be discussed in our contribution.

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